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# Spectroscopic, synthesis studies and evaluation of the biological activity of some new-3-(2hydroxy benzylidene) amino)-2-phenyl quinazolin-4(3H)- one Schiff base complexes

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## Abstract

This research includes the synthesis of a number of new complexes of some transition elements such as Co(II), Ni(II), Cu(II) and non-transition elements Zn(II), Cd(II), Hg(II) with the ligands of Schiff bases resulting from the condensation reaction between Salicylaldehyde and 3-amino-2-phenylquinazolin-4(3H)-one.

The ligand and its complexes were studied and diagnosed through molar electrical conductivity, magnetic susceptibility measurements, electronic spectra, infrared spectra, proton nuclear magnetic resonance spectroscopy, gas chromatography-mass spectrometry, and biological activity of the ligand and some of its complexes has been studied. It was shown through the study that the ligand gives neutral, non-electrolytic complexes that have the chemical formula [M(HBAPQ)$Cl_2$] and [Co$(HBAPQ)_2$)$Cl_2$] as:

M = Ni(II),Cu(II), Zn(II),Cd(II),Hg(II)

HBAPQ = (E)-3-((2-hydroxybenzylidene)amino)-2-Phenylquinazolin-4(3H)-one

The values of the electronic spectra and magnetic susceptibility measurements showed that the prepared complexes were tetracoordinate tetrahedral geometry, except for the cobalt (II) complex, which was hexacoordinate octahedral geometry.

**Keywords:** transition element complexes, quinazoline Schiff base ligands, quinazolinone complexes.

## Introduction

Quinazoline is a heterocyclic compound, as it is one of the most commonly used heterocyclic compounds in the fields of medical and pharmaceutical research (1,2), as it contains two nitrogen atoms whose formula consists of two fused aromatic rings, one of which is a benzene ring. The other is a pyrimidine ring (3,4). It is considered a distinct structure for drug development (5), which increases research activity in this field as part of our research on the synthesis of heterocyclic compounds (6-8), the Schiff base ligand, which contains a part of the quinazolinone, is reacted with some chlorides of divalent transition and non-transition elements to prepare coordination complexes (9, 10). In recent years (11), Schiff bases have shown a wide range of biological activities, including antitumor (12), anticancer (13), antibacterial (14), and antioxidant (15, 16) activities. Schiff bases are ligands important in coordination chemistry (17, 18). It is generally used to synthesize many complexes with metal ions because of their ability to coordinate (19). However, the stability of Schiff base complexes depends on many factors, as the more coordination number, the more stability of the complex (20, 21). One of their characteristics is that they are often colored and can form colored complexes with most transition metal ions (22), and Schiff bases have many applications, as they are used in chemical, industrial, medical, and agricultural fields (23, 24), they are also used as analytical reagents in diagnosis and quantitative analysis (25, 26), and is used in the manufacture of inks and dyes (27), antioxidant and reduction substances (28), and has effectiveness against cancer and in the pharmaceutical industry (29). In this study, Schiff base ligand (HBAPQ) complexes were prepared from (E)-3-((2-hydroxy benzylidene)amino)-2-Phenylquinazolin-4(3H)-one with chlorides of the transition and non-transition metal elements Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and diagnosed using physical, chemical and spectroscopic methods to obtain the structure of the complexes.

## Experimental

### Materials and methods

The chemicals are all of high purity as they were used without purification. The melting points or decomposition temperatures were recorded using an Electro

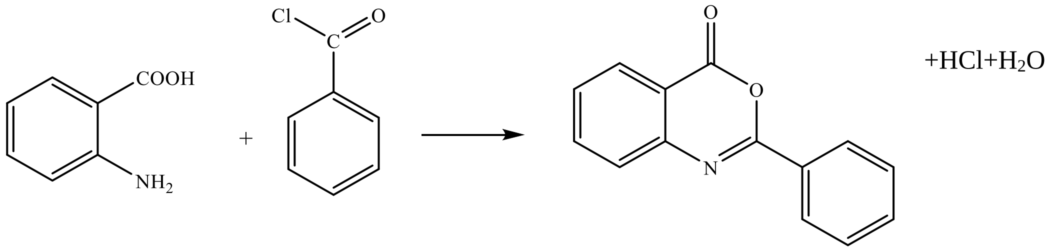
Thermal IA1900 Melting point Apparatus Type/SMP 30 device equipped by the British company Stuart in the Chemistry Department/College of Education for Girls/University of Mosul. The molar electrical conductivity solution of the prepared complexes was measured using a HANNA EC214 conductivity meter instrument of Italian origin and using dimethyl sulfoxide as solvent (DMSO) with a concentration of $10^{-3}$ molar at 25°C in the Chemistry Department/College of Education for Girls/University of Mosul.

The ligand and the prepared complexes' micro elemental analysis (CHN) were also recorded using the Euro Vector S.P.A Euro CHNSO Analyzer i2391: instrument EA 3000, Italian manufacture, at the University of Tehran, Iran. The UV-Vis spectra of the prepared solutions of ligands and complexes were recorded using Shimadzu UV-180-UV-Vis-spectrophotomer at a concentration of $10^{-3}$ molar and at 25°C using dimethyl sulfoxide (DMSO), quartz cells with a thickness of (1 cm) were used in the laboratory of Department of Chemistry /College of Education for Girls/University of Mosul. The magnetic susceptibility of the prepared complexes was measured at 25°C using a Sherwood Scientific MSB MK1 Magnetic Susceptibility Balance device in the Department of Chemistry/College of Education of Pure Science/ University of Tikrit. The infrared spectra of the prepared compounds were also measured using a Shimadzu FTIR 8400 S spectrometer at the Department of Chemistry/College of Science/Tikrit University, in the region between 4000-400 $cm^{-1}$ in terms of wavenumber using KBr discs. $^1$HNMR spectra of ligands and some prepared complexes were measured using the Bruker DRX system 400MHz using Tetramethyl silane (TMS) as an internal standard and dimethyl sulfoxide (DMSO-d6) solvent at the College of Science/University of Basra. The mass spectrum was measured to determine the molecular weight of the ligand and some complexes using a Gas Chromatography-Mass Spectrometry Measurement device, type GC-MS-QP2010Ultra, equipped by the Japanese company Shimadzu, in the Central Laboratory/College of the Applied Science/ University of Samarra. The culture medium and dishes were sterilized from bacteria using a Hirayama device of Japanese origin in the Department of Biology/ College of Education for Girls/ University of Mosul.

## Preparation of starting materials:

### 1- Preparation of the compound 2-phenyl-4H-1,3-benzoxazine-4-one

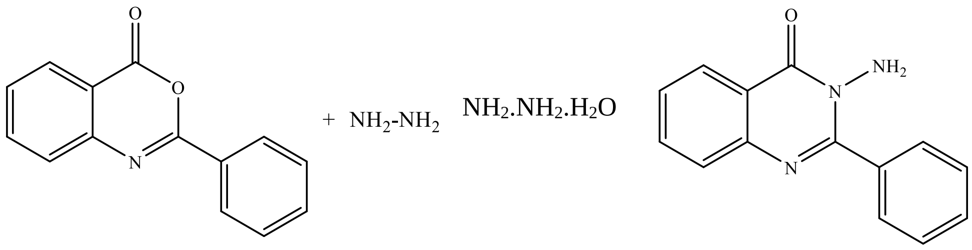
(1.71 g, 0.0125 mol) Anthranilic acid was taken in a round flask, and 15 ml of pyridine was added to it in an ice bath using a magnetic stirring device. (3.50 g, 0.025 mol) benzoyl chloride was added to the round flask drop by drop, then the mixture was cooled. The mixture was stirred for three hours until a precipitate formed, then the precipitate was filtered, washed well with water, recrystallized from ethanol, and dried under vacuum pressure. The following equation explains the reaction:



2-phenyl-4*H*-1,3-benzoxazine-4-one

### 2- Synthesis of the compound 3-amino-2-phenyl-4-quinazolinone

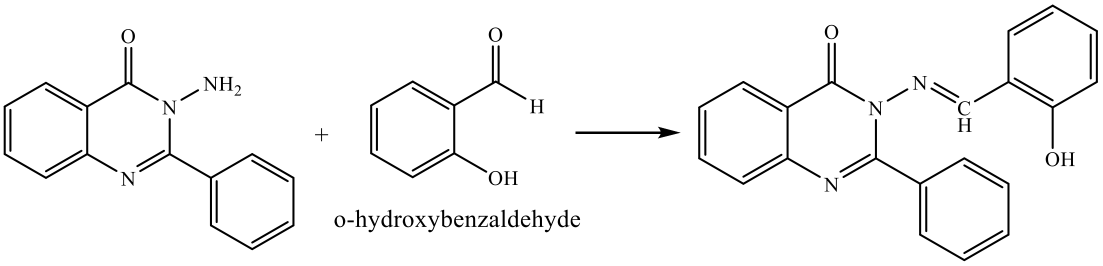
(2.78g, 0.0125mol) the compound (2-phenyl-4H-1,3-benzoxazine-4-one) was taken in a round flask, then 4ml of hydrazine dihydrate (85%) was added drop by drop, and 10ml of ethanol was added. The mixture was stirred using a magnetic stirrer, it was sublimated at 117°C for three hours, then the precipitate was cooled, filtered, recrystallized from ethanol, and then dried under vacuum pressure. The following equation explains the reaction:



3-amino-2-phenyl-4-quinazolinone

### 3- Synthesis of the ligand (E)-3-((2-hydroxybenzylidene)amino)-2-Phenylquinazolin-4(3H)-one :

(2.69g, 0.0125mol) of the compound (3-amino-2-phenyl-4-quinazolinone) was dissolved in 20ml of absolute ethanol, and (1.52g, 0.0125mol) of (o-hydroxybenzaldehyde) was added with the addition of drops of glacial acetic acid. The mixture was heated by reflux for 6 hours, then cooled in an ice bath to complete the precipitation process. The precipitate was filtered, dried, and recrystallized from ethanol. The following reaction explains the synthesis of the ligand:



o-hydroxybenzaldehyde

3 3-amino-2-phenylquinazolinone

(*E*)-3-((2-hydroxybenzylidene)amino)-2-phenylquinazolin-4(3*H*)-one

## Synthesis of complexes

The complexes were prepared by reacting metal (II) chloride with the prepared ligand using the following method: (0.005mol, 1.70g) or (0.01mol, 3.41g) of the prepared ligand was dissolved in 10ml of hot absolute ethanol, then (0.005mol) of metal chloride in 10ml of absolute ethanol are added to it, provided that the addition continues for 10-20 minutes with continuous stirring. The mixture is heated by reflux for 3 hours. The mixture is cooled in an ice bath, then the precipitate is filtered, washed with cold absolute ethanol and diethyl ether several times, and dried in an electric oven at (50-60 °C). Table (1) shows some physical properties of the prepared ligand and complexes.

**Table 1: Physical properties and microanalysis of the prepared ligands and complexes**

| **No.** | **Compound** | **Colour** | **M.p.°C** | **Yield%** | **$\Lambda_{M(DMSO)}$ $cm^2.ohm^{-1}.mol^{-1}$** | **Analysis Calc. (Found)** | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | **C%** | **H%** | **N%** |
| - | HBAPQ | White | 227-230 | 95 | - | 71.15<br>(70.75) | 4.58<br>4.65)( | 11.32<br>(12.25) |
| 1 | $[Co(HBAPQ)_2Cl_2]$ | Orange | 223-225 | 81 | 12.7 | 53.60<br>(54.11) | 3.18<br>(3.42) | 8.92<br>(9.08) |
| 2 | $[Ni(HBAPQ)Cl_2]$ | Yellowish green | 240-243 | 79 | 19.8 | 53.50<br>(54.02) | 3.188<br>(3.33) | 8.92<br>(8.11) |
| 3 | $[Cu(HBAPQ)Cl_2]$ | turquoise blue | 355-359 | 81 | 10.9 | 53.01<br>(52.78) | 3.15<br>(3.50) | 8.83<br>(8.56) |
| 4 | $[Zn(HBAPQ)Cl_2]$ | Pale yellow | 207-209 | 68 | 14.3 | 52.80<br>(53.32) | 3.14<br>(3.30) | 8.80<br>(9.02) |
| 5 | $[Cd(HBAPQ)Cl_2]$ | Off white | 213-215 | 65 | 10.4 | 48.07<br>(47.92) | 2.86<br>(3.09) | 8.01<br>(8.95) |
| 6 | $[Hg(HBAPQ)Cl_2]$ | White | 234-235 | 70 | 21.4 | 41.15<br>(41.79) | 2.44<br>(2.77) | 6.85<br>(6.58) |

## Results and discussion:

Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Mercury(II) with Schiff base ligand (E)-3-(2-hydroxy benzylidene-2-phenyl quinazolin-4(3H)-one were prepared, characterized and studied, by reacting the ligand with the metal chlorides mentioned above, in order to form metal complexes as shown by the following two chemical equations:

$MCl_2.nH_2O + HBAPQ \longrightarrow [M(HBAPQ)Cl_2] + nH_2O$

$Co\ Cl_2.6H_2O + 2(HBAPQ) \longrightarrow [Co\ (HBAPQ)_2Cl_2] + 6H_2O$

M= Ni(II),Cu(II),Zn(II),Cd(II) or Hg(II)

n=0,2,6

The results of the elemental analysis (C.H.N.) enhanced the results of the reaction in the above equations, and showed that the molar ratio (1:1) and (1:2) (metal-ligand) and the complexes formed are all solid, colored, stable substances at room temperature, insoluble in water, and slightly soluble in ethanol and methanol, and have high solubility in solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). It was demonstrated through molar electrical conductivity measurements of the prepared complexes, at a concentration of ($10^{-3}$M) and using the solvent dimethyl sulfoxide (DMSO) when the solution is in thermal equilibrium at a temperature (25°C), that the complexes are consistent with the proposed structural formulae, and that the complexes fall within neutral, non-electrolytic behavior (30,32) Table (1) and Figures (1-7). The coordination sites of the prepared Schiff base ligand and complexes in this study were determined by infrared spectra. The spectrum showed the stretching frequency of the ligand and the groups: ν (C=N), ν (C=O), ν (OH), ν (M-N), ν (M-O), as well as the bending frequency of the phenolic hydroxyl group δ (OH), and the changes occurring in the infrared spectra of the complexes are affected by the coordination of the ligand with the metal atoms of its donor atoms (33), as the stretching frequency of the azomethine group of the ligand appeared in the region (1651 $cm^{-1}$), and when it binds with the metal, it shifts to a lower frequency (1583-1618$cm^{-1}$), which indicates the coordination of the azomethine group with the metal ions due to the weakness that occurs in the double bonding of the azomethine group (34-36). The stretching frequency of the hydroxyl group ν(OH) appeared as a band for the prepared ligand in the region (3282$cm^{-1}$), while the band located in the region (1356$cm^{-1}$) belongs to the bending frequency of the hydroxyl group δ(OH) (37-

39). The stretching and bending frequency bands of the ν(OH), δ(OH) group appeared in lower regions than those observed for the ligand in the region confined between (3201-3284 $cm^{-1}$) and (1331-1356 $cm^{-1}$) respectively, which confirms the coordination of the metal ions with the oxygen atom of the hydroxyl group (37, 38). The ligand spectrum showed an absorption band for the stretching frequency of the aromatic bond ν(CH) at a frequency (3053$cm^{-1}$). However, when forming the complexes, this band appeared close or fixed (3055-3064 $cm^{-1}$), which indicates that this group does not participate in coordination with any metal ions in the prepared complexes (40, 41). The stretching frequency of the ν(C=O) bond appeared in the region (1666 $cm^{-1}$), and when the complexes were formed, the band appeared in a close or fixed region (1651-1672 $cm^{-1}$), which indicates that this group does not participate in coordination with the metal ions of the prepared complexes (42).The stretching frequency of the ν(M-N), ν(M-O) bonds appeared in the low frequency region of the infrared spectrum of complex compounds, and these frequencies are not observed in the ligand spectrum, as the infrared spectrum showed the stretching of the ν(M-N) and ν(M-O) groups of the prepared complexes in the region confined between (442-484 $cm^{-1}$) and (511-588 $cm^{-1}$) respectively, which confirms their appearance in the prepared complexes and their non-appearance in the ligand spectrum within the range specified above on the coordination of metal ions and the ligand through the azomethine nitrogen atom and the phenolic hydroxyl oxygen atom, and this agrees with what has been published in research (43, 44) Table (2). The stretching frequency of the (M-Cl) bond appears a; this-280 $cm^{-1}$), this frequency was not observed in the infrared spectrum for the chlorine ions that are coordinated to the metal ions located inside the coordination sphere because they are outside the range of the device used. Their coordination was deduced through the molar conductivity of solutions of the prepared complexes, as well as bas andic measurements and electronic spectra of the prepared complexes (37, 38, 45).

### Table (2) Important frequency values in the IR spectrum for ligands and complexes (cm$^{-1}$)

| Comp. | ν(C=O) | ν(C=N) | $\nu(C=N)_{ring}$ | ν(OH) | δ(OH) | $\nu(C=C)_{ar}$ | ν(N-N) | $\nu(CH)_{ar}$ | $\nu(CH)_{al}$ | ν(M-N) | ν(M-O) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HBAPQ | 1666 | 1651 | 1583 | 3282 | 1356 | 1606 | 1030 | 3053 | 2880 | - | - |
| [Co(HBAPQ)Cl$_2$] | 1653 | 1584 | 1585 | 3202 | 1356 | 1606 | 1032 | 3035 | 2854 | 445 | 513 |
| [Ni(HBAPQ)Cl$_2$] | 1664 | 1583 | 1587 | 3215 | 1331 | 1606 | 1030 | 3055 | 2854 | 484 | 513 |
| [Cu(HBAPQ)Cl$_2$] | 1672 | 1618 | 1549 | 3236 | 1346 | 1593 | 1047 | 3064 | 2887 | 457 | 540 |
| [Zn(HBAPQ)Cl$_2$] | 1653 | 1585 | 1524 | 3200 | 1321 | 1606 | 1030 | 3053 | 2856 | 443 | 588 |
| [Cd(HBAPQ)Cl$_2$] | 1653 | 1583 | 1526 | 3208 | 1317 | 1606 | 1031 | 3055 | 2854 | 442 | 513 |
| [Hg(HBAPQ)Cl$_2$] | 1651 | 1584 | 1528 | 3202 | 1317 | 1606 | 1030 | 3055 | 2858 | 445 | 511 |

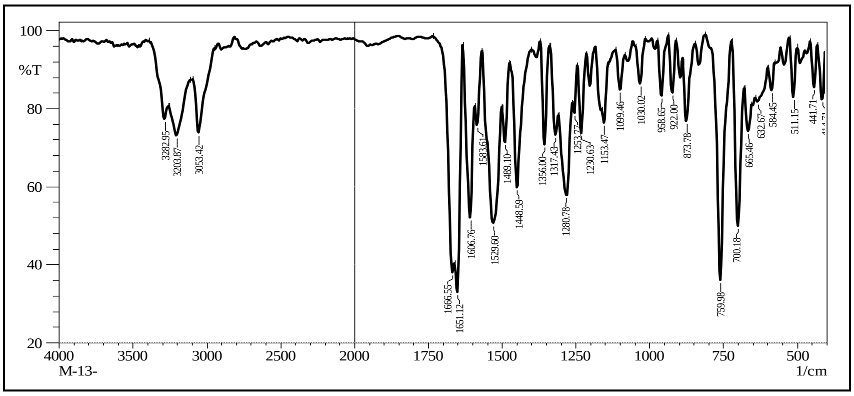


Figure (1): Infrared spectrum of HBAPQ ligand

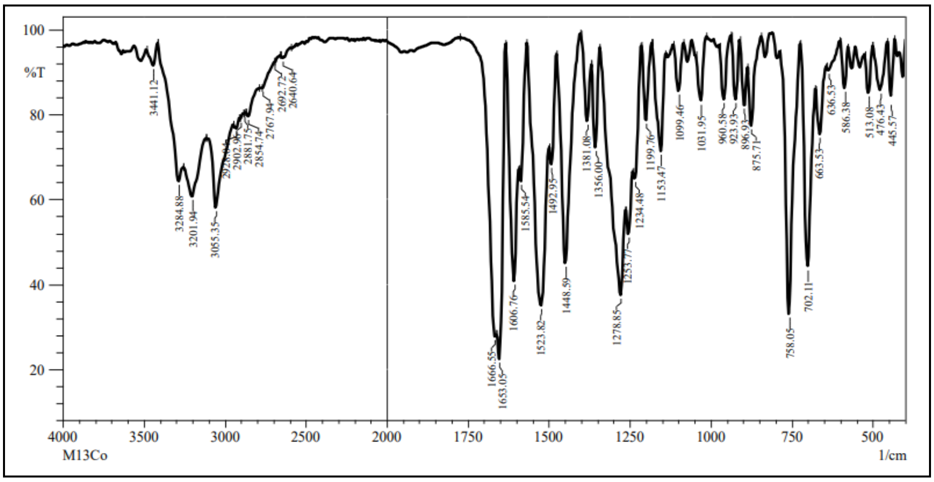


**Figure (2): Infrared spectrum of the complex [Co(HBAPQ)$_2$Cl$_2$]**

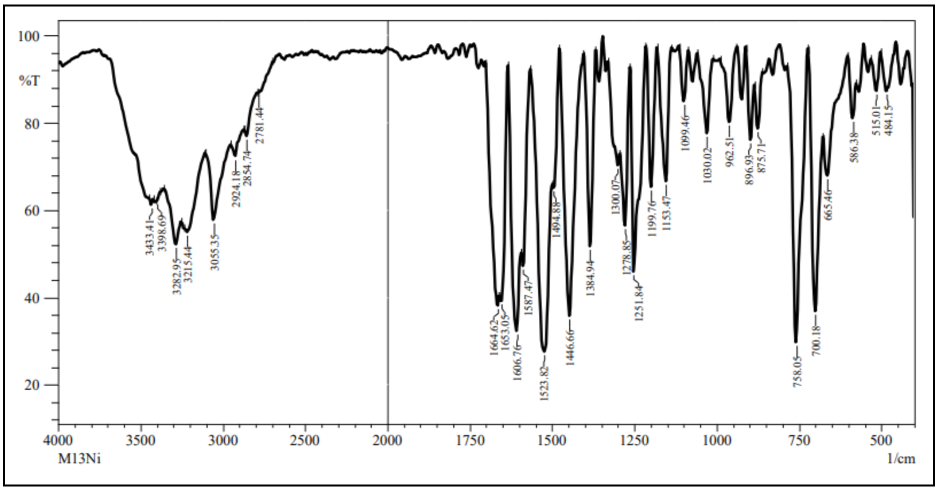


**Figure (3): Infrared spectrum of the complex [Ni(HBAPQ)Cl$_2$]**

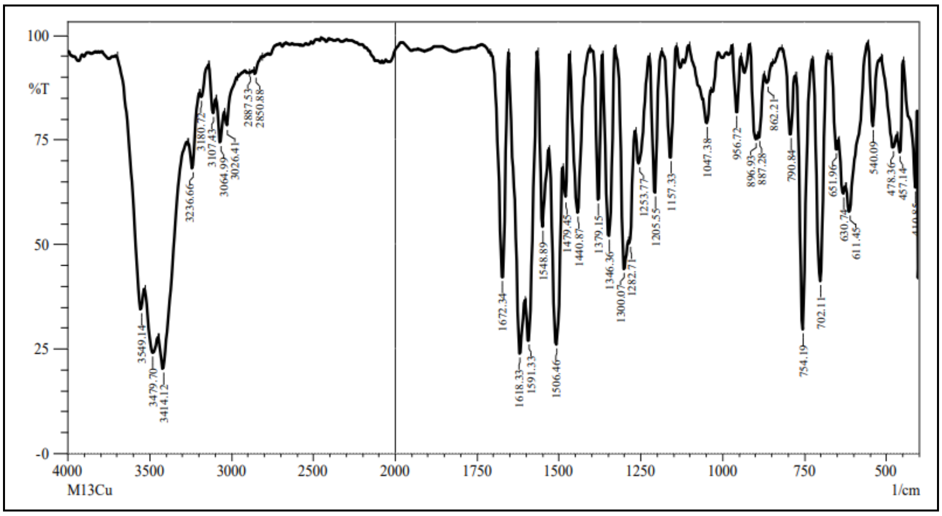


**Figure (4): Infrared spectrum of the complex [Cu(HBAPQ)Cl$_2$]**

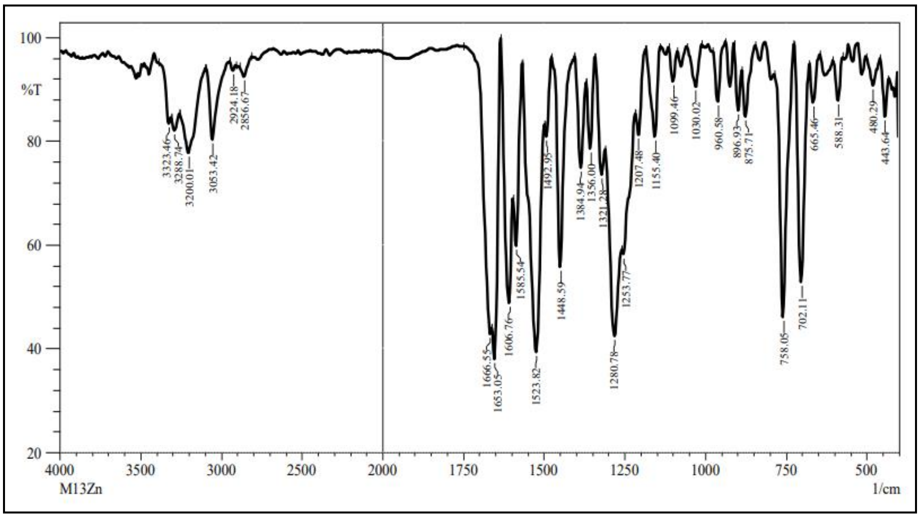


Figure (5): Infrared spectrum of the complex [Zn(HBAPQ)Cl₂]

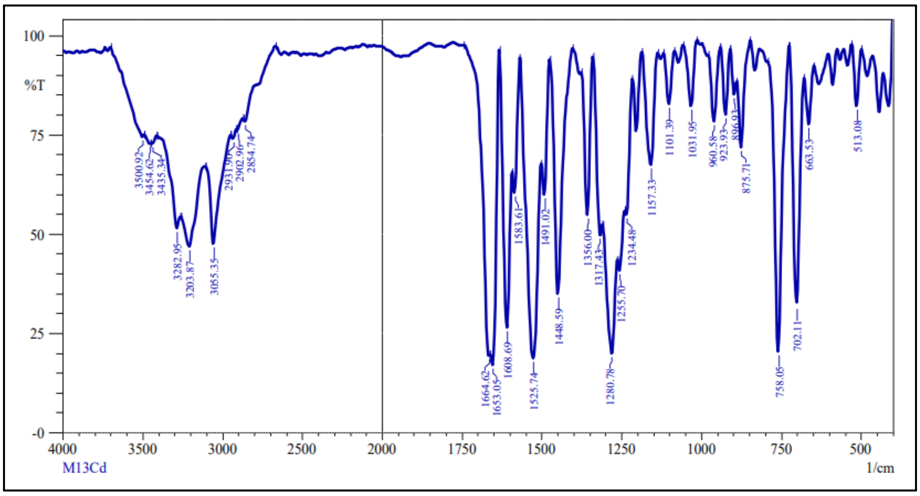


Figure (6): Infrared spectrum of the complex [Cd(HBAPQ)Cl₂]

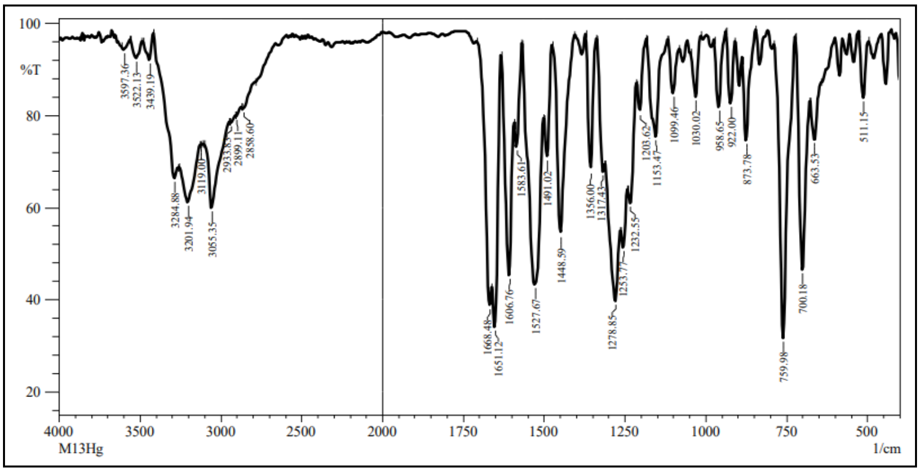
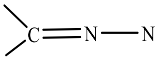


Figure (7): Infrared spectrum of the complex [Hg(HBAPQ)Cl₂]

The magnetic susceptibility of the complexes prepared at 25°C was measured using Gouy method (46, 47). The Co(II) complex showed a magnetic moment with a value of (5.09 B.M.), which is due to three unpaired electrons, and this is consistent with the value of the magnetic moment for cobalt (II) complexes with an octahedral structure (48,49). In comparison, the prepared nickel (II) complex showed a magnetic moment value of (4.01 B.M.) due to the presence of two unpaired electrons, which is greater than the theoretical value (2.83 B.M.) due to the presence of an orbital contribution, it agrees with the value of the magnetic moment for tetrahedral nickel (II) complexes (38, 48). As for the copper (II) complex, it showed a magnetic moment value (2.03 B.M.), and this value corresponds to the electronic spectrum of the complex, which has a tetrahedral structure (49). All complexes of Zn(II), Cd(II), and Hg(II) are diamagnetic because they have an orbital filled $d^{10}$, with electrons and take the most common tetrahedral structure, based on the results of chemical analysis and physical measurements, Table 3 (50-52).

As for the electronic spectra, they were measured for the ligand and complexes at a concentration of ($10^{-3}$M) and a temperature of (25°C) using dimethyl sulfoxide (DMSO) solvent, Table (3). The prepared ligand (Figure 8) showed two main bands, where the first band appeared at 36231 $cm^{-1}$ and is attributed to the electronic transition ($\pi \rightarrow \pi^*$), which is attributed to the chromophore (  ), and the second band appeared at 34965 $cm^{-1}$ and is attributed to the electronic transition ($n \rightarrow \pi^*$). This transfer occurs due to the nitrogen and oxygen atoms in the ligand structure (53). The Co(II) complex (Figure 9) showed absorption bands at (14869, 16260, 25031 $cm^{-1}$), which are attributed to electronic transitions (54):

$\nu_1$ $^4T_1\,g(F) \longrightarrow {}^4T_2\,g(F)$
$\nu_2$ $^4T_1\,g(F) \longrightarrow {}^4A_2\,g(F)$
$\nu_3$ $^4T_1\,g(F) \longrightarrow {}^4T_2\,g(P)$

The charge transfer (C.T) band appeared at (30441 $cm^{-1}$), which confirms that the cobalt (II) complex has a highly spin-twisted octahedral structure (55, 56).

As for the nickel (II) complex, the electronic spectrum (Figure 10) showed that it has an absorption band at (13253 $cm^{-1}$) due to the electronic transition:

$\nu_3$ $^3T_1(F) \longrightarrow {}^3T_1(P)$

As for the two bands that belong to the two electronic transitions:

$\nu_1$ $^3T_1(F) \longrightarrow {}^3T_2(F)$
$\nu_2$ $^3T_1(F) \longrightarrow {}^3A_1(F)$

They were not diagnosed due to their low intensity, as they were outside the range of the device used (57), and the charge transfer (C.T) band has a value of (31298 $cm^{-1}$). These values agree with magnetic measurements and, therefore, correspond with the tetrahedral arrangement of the Ni(II) complex (58, 59). The electronic spectrum (Figure 11) of the copper complex Cu(II) was measured. It was observed a broad absorption band in the region (14992 $cm^{-1}$) due to the electronic transition $^2T_2(D) \rightarrow {}^2E(D)$ and the charge transfer band at (30950 $cm^{-1}$), which is consistent with magnetic measurements of the complex and with published research indicating that it adopts a tetrahedral structure (60, 61). As for the Hg(II), Cd(II), and Zn(II) complexes (Figures 12 and 13), they gave absorption bands at (30211-31948 $cm^{-1}$); these absorptions most likely represent charge transfer spectra and in a few cases are attributed to ligand bands, as these absorptions do not give (d-d) transitions because they have a $d^{10}$ orbital in the outer valence orbital. These complexes took the structure of a tetrahedral (53, 62, 63). Table (3) shows the electronic transitions in the UV-Vis spectrum and the magnetic moments of the prepared ligands and complexes.

**Table (3) Electronic spectra ($cm^{-1}$) and magnetic moments (B.M.) of the prepared compounds**

| No. | Compound | Absorption region ($cm^{-1}$) | Possible assignments | eff (B.M.)μ | Chemical structure |
|---|---|---|---|---|---|
| - | HBAPQ | **36231**<br>**34965** | $^{*}\pi\pi$-<br>$^{*}\pi n$- | - | - |
| 1 | $[Co(HBAPQ)Cl_2]$ | **14869**<br>**16260**<br>**25031**<br>**30441** | $^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(F)$<br>$^{4}T_{1}g(F) \rightarrow {}^{4}A_{2}g(F)$<br>$^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(P)$<br>**Chargetrasfer (C.T)** | **5.09** | $O_h$ * |
| 2 | $[Ni(HBAPQ)Cl_2]$ | **13253**<br>**31298** | $^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$<br>**Chargetrasfer (C.T)** | **4.01** | $T_d$ ** |
| 3 | $[Cu(HBAPQ)Cl_2]$ | **14992**<br>**30950** | $^{2}T_{2}(D) \rightarrow {}^{2}E(D)$<br>**Chargetrasfer (C.T)** | **2.03** | $T_d$ |
| 4 | $[Zn(HBAPQ)Cl_2]$ | **31948** | **Chargetrasfer (C.T)** | **Diamagnetic** | $T_d$ |
| 5 | $[Cd(HBAPQ)Cl_2]$ | **30211** | **Chargetrasfer (C.T)** | **Diamagnetic** | $T_d$ |
| 6 | $[Hg(HBAPQ)Cl_2]$ | **30216** | **Chargetrasfer (C.T)** | **Diamagnetic** | $T_d$ |

* $O_h$= Octahedral from group theory

** $T_d$ = Tetrahedral from group theory

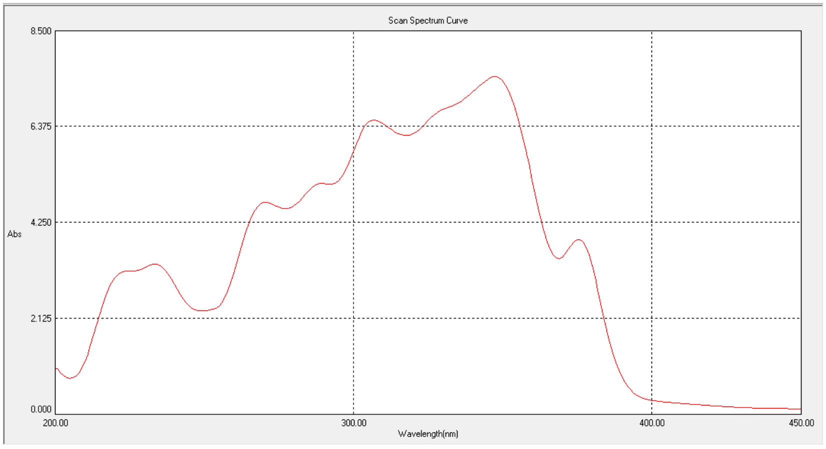


Figure (8): UV-Vis spectrum of the ligand (HBAPQ)

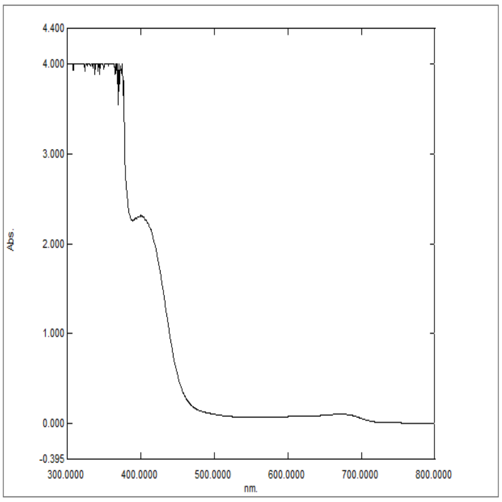


Figure (9): UV-Vis spectrum of the complex [$Co(HBAPQ)_2Cl_2$]

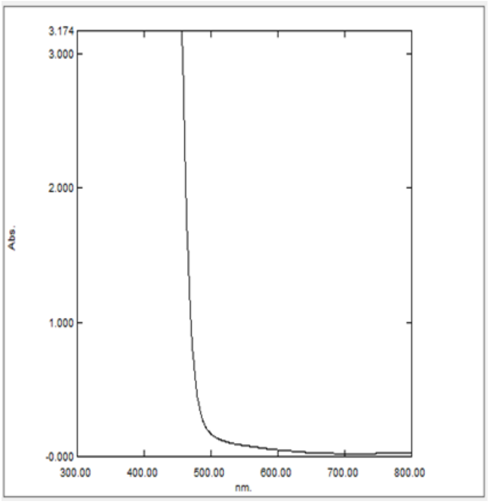


Figure (10): UV-Vis spectrum of the complex [$Ni(HBAPQ)Cl_2$]

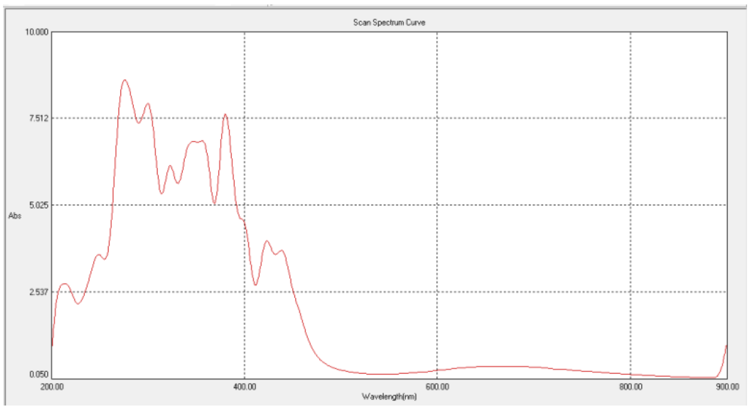


**Figure (11): UV-Vis spectrum of the complex [Cu(HBAPQ)$Cl_2$]**

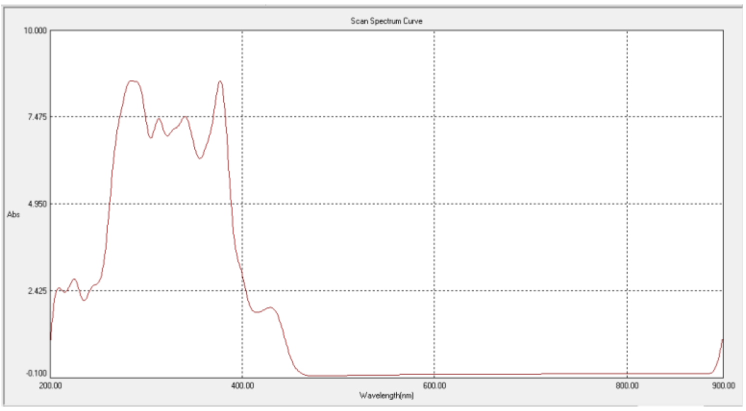


**Figure (12): UV-Vis spectrum of the complex [Zn(HBAPQ)$Cl_2$]**

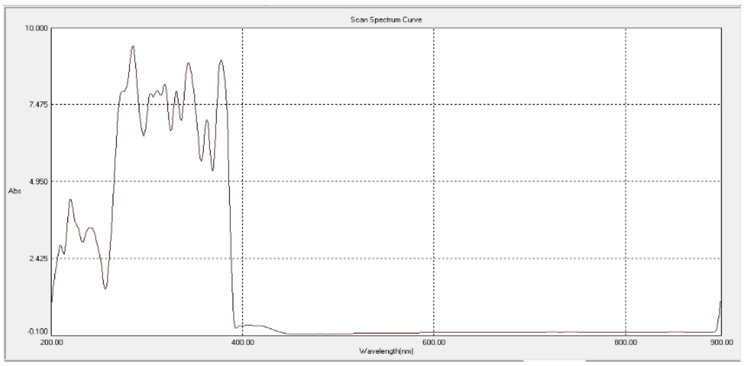


**Figure (13): UV-Vis spectrum of the complex [Cd(HBAPQ)$Cl_2$]**

In this study, $^1$H-NMR spectroscopy was used to study the structural characteristics of the ligand (HBAPQ) and complexes (4) and (5), Figures (14-16), using (DMSO-d6) solvent and the reference is tetramethyl silane ($SiMe_4$), and verify its chemical formula by relying on the values of chemical shifts and integration as shown in Table (4), as the $^1$H-NMR spectrum of the proton for the ligand showed a single signal at (δH 8.70 ppm 1H) that belongs to one proton of the azomethine group (-N=CH). Also, a single signal appeared at (δH 11.15 ppm 1H) that belongs to one proton of the phenolic hydroxyl group OH, and a multiple signal appeared at (δH 6.83-8.59 ppm 13H) belongs to the protons of the aromatic rings.

The proton $^1$H-NMR spectrum of the Zn(II) complex (4) showed the protons of the aromatic ring in the form of a multiple signal between (δH 6.90-8.58 ppm 13H), which refers to 13 protons, and a signal appeared belonging to the azomethine group at (δH 8.69 ppm 1H) for one proton, and the signal of the phenolic hydroxyl group appeared at (δH 11.14 ppm 1H) due to one proton.

As for the Cd(II) complex (5), it showed a multiple signal from (δH 8.57-6.90 ppm 13H) that belongs to the protons of the aromatic rings, while the signal for the azomethine group appeared at (δH 8.69 ppm 1H), which belongs to one proton. As for the phenolic hydroxyl group (OH) appeared at (δH 11.13 ppm 1H) due to one proton.

**Table (4) $^1$H-NMR spectrum data for the prepared compounds**

| Compound | |
|---|---|
| HBAPQ | δ11.15 (s.1H, OH), δ6.83 -8.59 (m, 13H, Ar-H), δ8.70 (s.1H, CH=N-) |
| [Zn(HBAPQ)$Cl_2$] | δ11.14 (s.1H, OH), δ6.90 -8.58 (m, 13H, Ar-H), δ8.69 (s.1H, CH=N-) |
| [Cd(HBAPQ)$Cl_2$] | δ11.13 (s.1H, OH), δ6.90 -8.57 (m, 13H, Ar-H), δ8.69 (s.1H, CH=N-) |

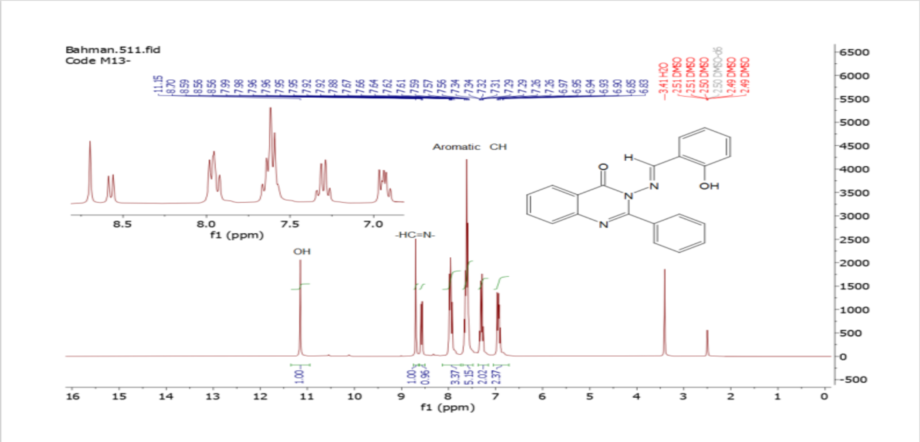


Figure (14): $^1$H-NMR spectrum of HBAPQ

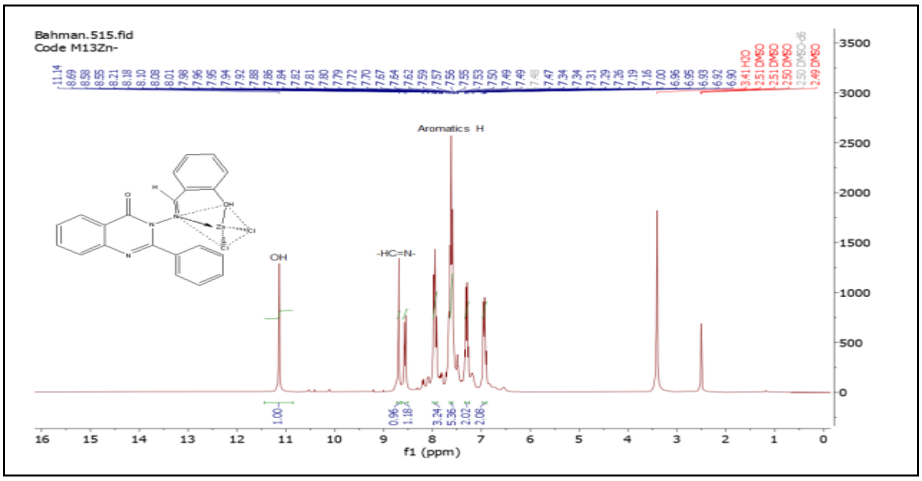


Figure (15): $^1$H-NMR spectrum of the complex [Zn(HBAPQ)$Cl_2$]

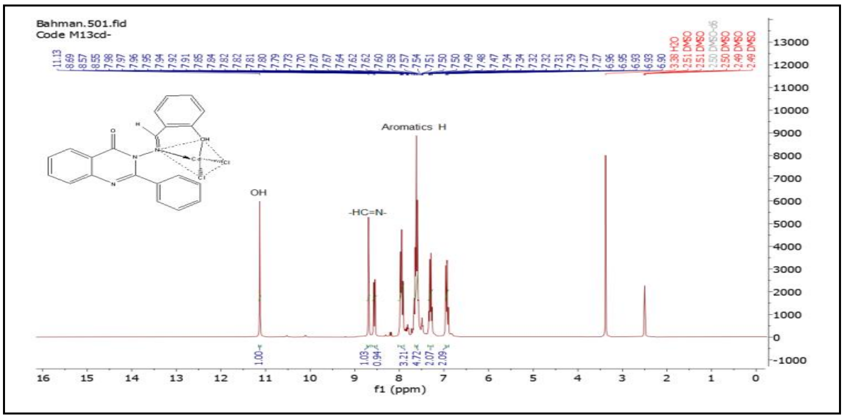
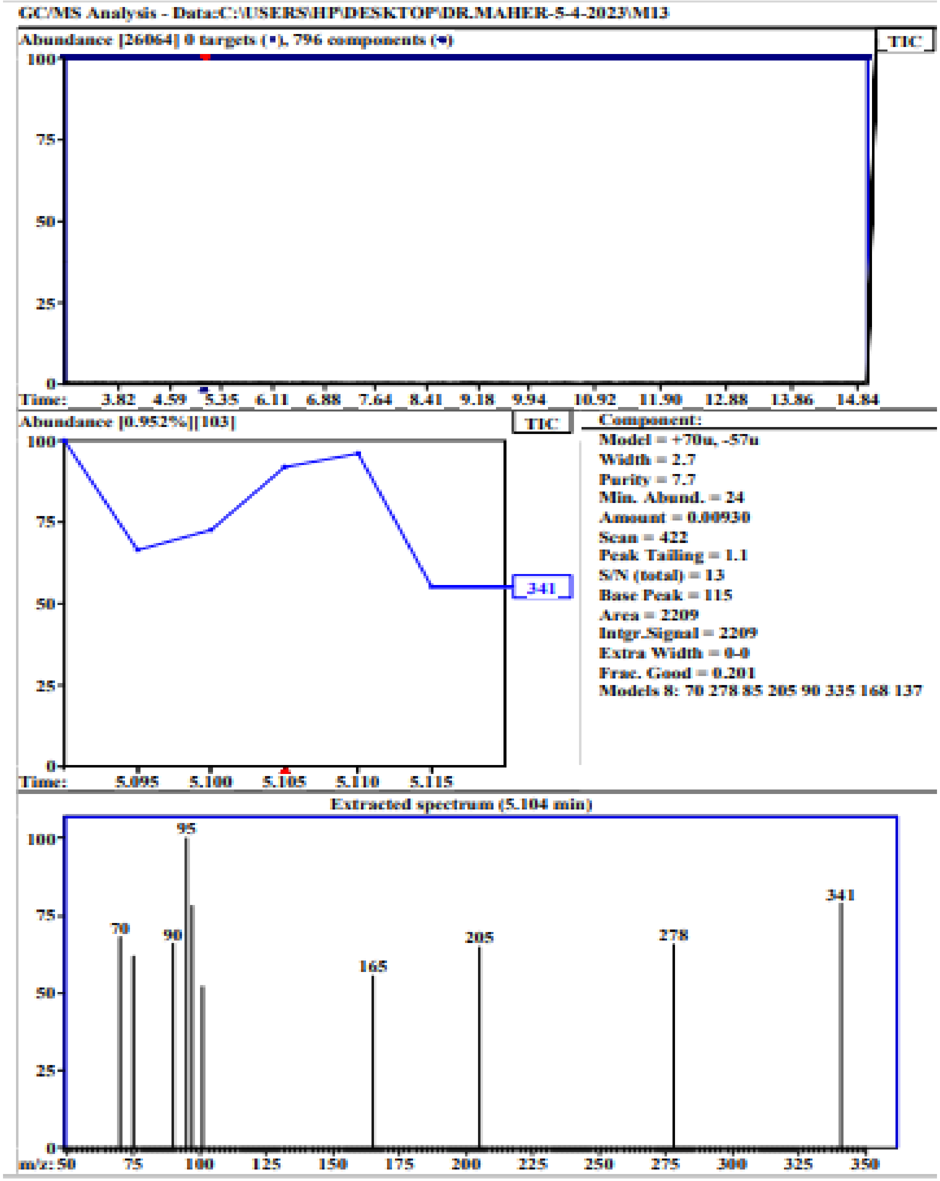


Figure (16): $^1$H-NMR spectrum of the complex [Cd(HBAPQ)$Cl_2$]

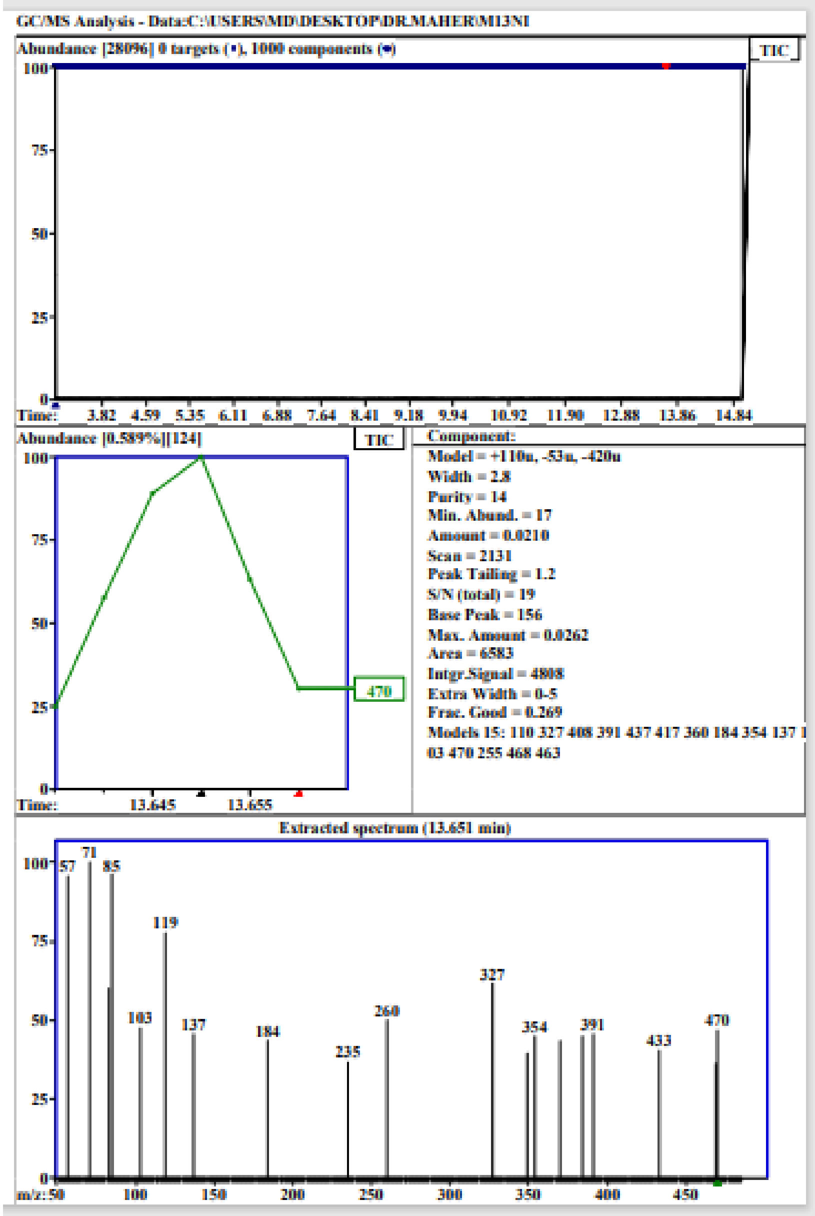
## Gas chromatography-mass spectrometry

Mass spectral data of the Schiff base ligand and Cu(II), complex are given in Fig. (17,18). Mass spectra of the two compound peaks with different relative masses, Show molecular ion. which are in good agreement with expected values.



```
Component:
Model = +70u, -57u
Width = 2.7
Purity = 7.7
Min. Abund. = 24
Amount = 0.00930
Scan = 422
Peak Tailing = 1.1
S/N (total) = 13
Base Peak = 115
Area = 2209
Intgr.Signal = 2209
Extra Width = 0-0
Frac. Good = 0.201
Models 8: 70 278 85 205 90 335 168 137
```

**Figure (17): Mass spectrum of HBAPQ**



Component:
Model = +110u, -53u, -420u
Width = 2.8
Purity = 14
Min. Abund. = 17
Amount = 0.0210
Scan = 2131
Peak Tailing = 1.2
S/N (total) = 19
Base Peak = 156
Max. Amount = 0.0262
Area = 6583
Intgr.Signal = 4808
Extra Width = 0-5
Frac. Good = 0.269
Models 15: 110 327 408 391 437 417 360 184 354 137
03 470 255 468 463

Figure (18): Mass spectrum of the complex [Ni(HBAPQ)$Cl_2$]

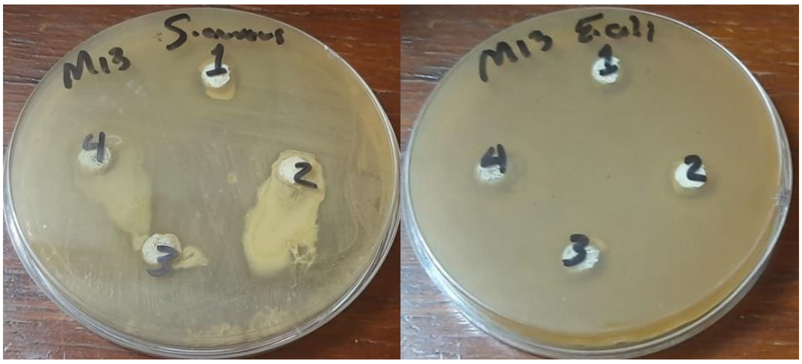
## Biological activity

The effect of the ligand (HBAPQ) and the complexes prepared in this research was studied on two species of bacteria: *Escherichia coli*, which is gram-negative and *Staphyl ococcusaureuse*, which is gram-positive, using dimethyl sulfoxide (DMSO) as a solvent in this study. The *E.coli* bacteria treats many infections, including the colon, as well as those affecting the bladder and urinary tract. As for the

*Staphylococcus aureus* bacteria, it is used to treat skin infections (64). A control model for the solvent was conducted and its effect on bacterial growth was studied under the same conditions to avoid solvent interference (65), also, a comparison was made with a type of antibiotic, namely (Imepinem), as shown in Table (5), which affects the complexes and the ligand of the prepared Schiff base on the two mentioned species of bacteria (66, 67), Figure (19) and Scheme (1,2). The study of the bacterial activity of the ligand and prepared complexes against these two species of bacteria (*Escherichia coli*, *Staphyl ococcusaureuse*) showed a variation in the activity of these compounds. The study showed that the best compounds were the copper (II) complex, followed by the ligand (68).

**Table (5): Inhibitory effectiveness of the prepared compounds on two species of the studied bacteria**

| **No.** | **Name** | **Inhibitory effect on *E. coli*** | | | | **Inhibitory effect on *staph. aureus*** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **12.5 mg/ml** | **25 mg/ml** | **50 mg/ml** | **100 mg/ml** | **12.5 mg/ml** | **25 mg/ml** | **50 mg/ml** | **100 mg/ml** |
| - | HBAPQ | 7.5 | 8 | 9.5 | 10.5 | 6.5 | 7.5 | 8 | 9 |
| 1 | [Ni(HBAPQ)$Cl_2$] | 0 | 0 | 8 | 10 | 7 | 8 | 9 | 11 |
| 2 | [Cu(HBAPQ)$Cl_2$] | 10 | 16 | 18 | 20 | 10 | 15 | 16.5 | 18 |
| 3 | [Zn(HBAPQ)$Cl_2$] | 0 | 0 | 7 | 8 | 0 | 0 | 0 | 0 |
| 4 | Imepinem | 12 | 12 | 12 | 12 | 13 | 13 | 13 | 13 |



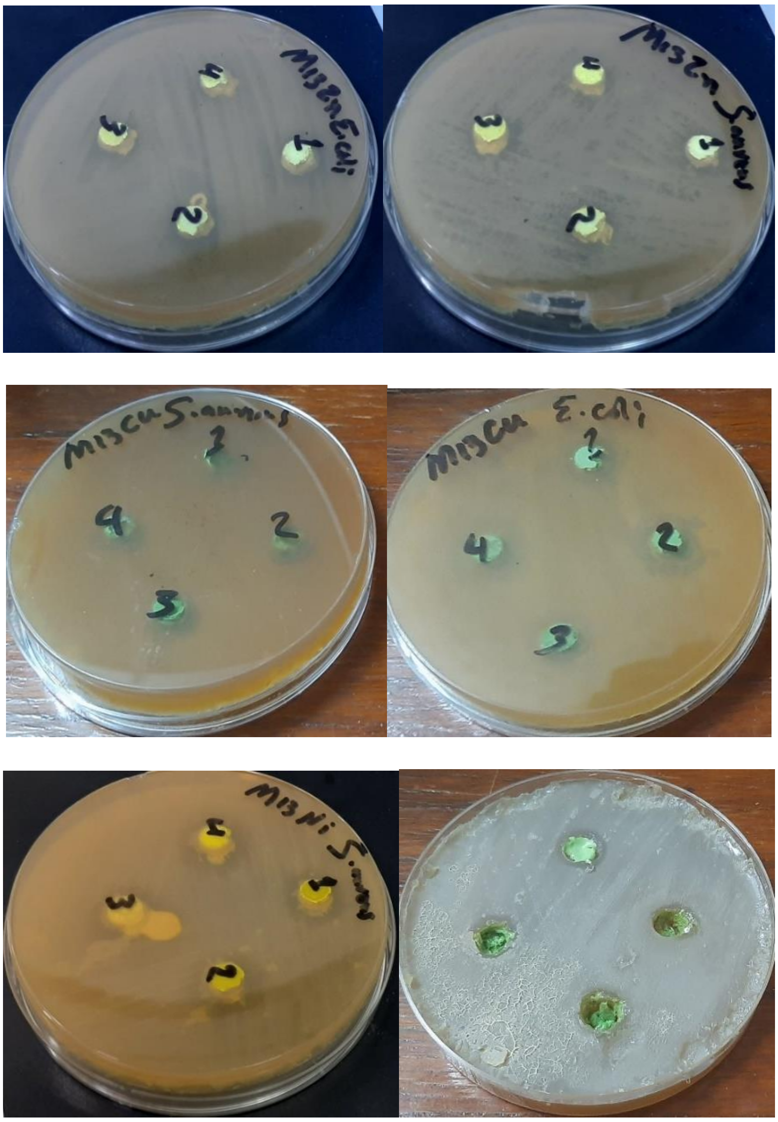
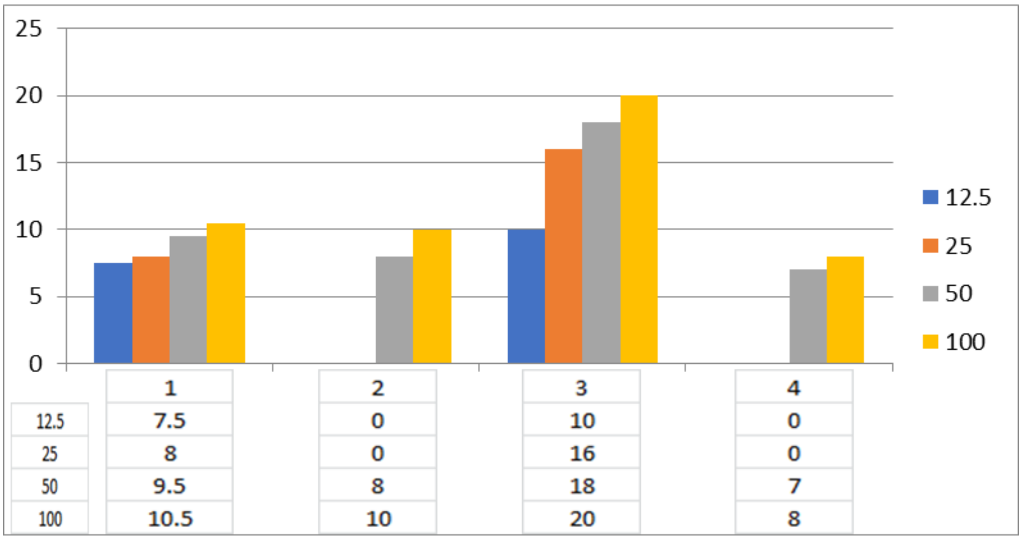
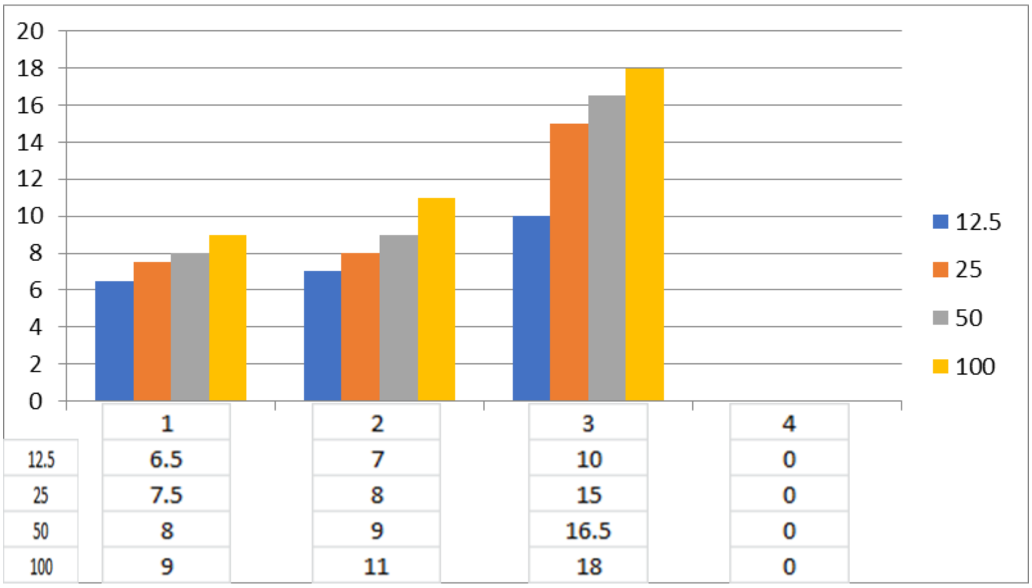


Figure (19): Inhibitory effectiveness of the prepared compounds on the growth of bacteria *E.coli, S.aureus*



| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| 12.5 | 7.5 | 0 | 10 | 0 |
| 25 | 8 | 0 | 16 | 0 |
| 50 | 9.5 | 8 | 18 | 7 |
| 100 | 10.5 | 10 | 20 | 8 |

**Scheme (1): The inhibitory effect of ligands and some prepared complexes on the growth of E.coli bacteria**

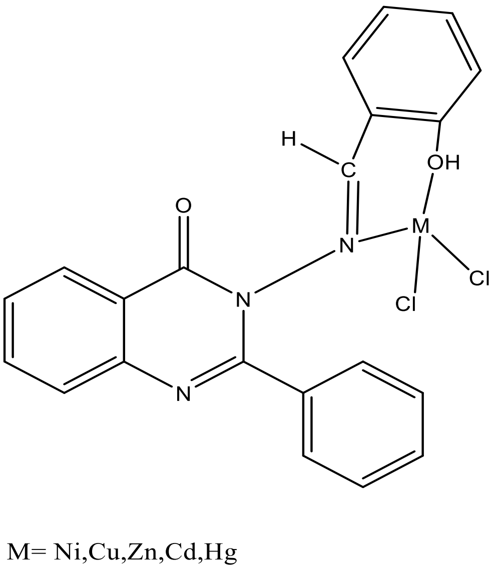


| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| 12.5 | 6.5 | 7 | 10 | 0 |
| 25 | 7.5 | 8 | 15 | 0 |
| 50 | 8 | 9 | 16.5 | 0 |
| 100 | 9 | 11 | 18 | 0 |

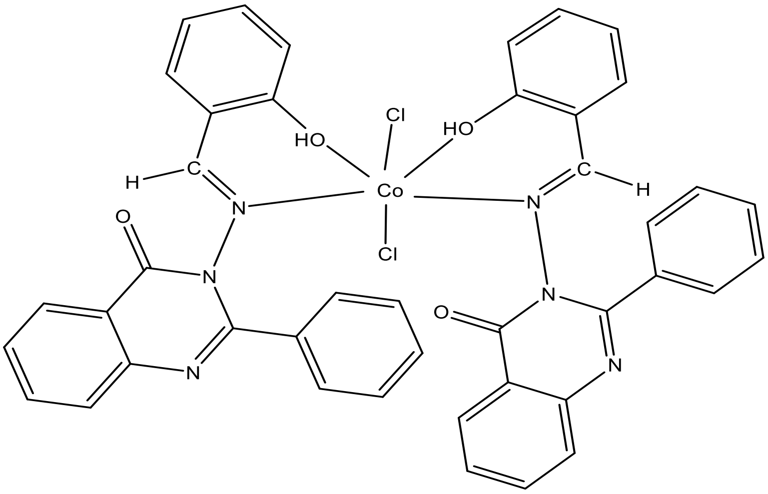
**Scheme (2): The inhibitory effect of ligands and some prepared complexes on the growth of S.aureus bacteria**

## Conclusions

From the various chemical, physical, and spectroscopic studies described above, it was concluded that the Schiff base ligand of the prepared (HBAPQ), gave stable complexes when it reacted with the metal ions used in this study, and it acts a bidentate manner through the nitrogen atom of the azomethine group and the oxygen atom of the phenolic hydroxyl group. From these measurements, it was suggested that the structure of all complexes takes a tetrahedral structure with tetracoordinated geometries, Figure (20), except for the cobalt (II) complex (1), has the octahedral structure and hexacoordinated geometry. A study evaluating the biological activity of the ligand and its complexes against two species of pathogenic bacteria (Gram positive and negative), *staph.aureas* and *E.coli*, showed that the ligand and complexes have high activity, but to varying degrees.



**(a) Tetrahedral ($T_d$)**



**(b) Octahedral ($O_h$)**

**Figure (20) Molecular structure of the prepared complexes**

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